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Evaluation of 1 percent Neutral Buffered Potassium Iodide Procedure for Calibration of Ozone Monitors

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16. ABSTRACT

The 1 percent neutral buffered potassium iodide procedure, as specified for calibration of ozone monitors in the Environmental Protection Agency (EPA) reference method for measurement of photochemical oxidants, was evaluated.

The procedure was found to be vulnerable to error in three major areas: 1) the time allowed for measurement of iodine absorbance, 2) purity of potassium iodide reagent, and 3) type of impinger used. Variations in results produced by minor changes within the specifications of the procedure suggest that the method is difficult to control.

Improved specifications and procedures were documented to minimize the effect of these parameters on results and to aid the user in proper use of the procedure. The improved procedure shows a positive bias of 7.5 ± 3.4 percent.

The Environmental Monitoring and Support Laboratory (EMSL), EPA, has decided that further work to improve the procedure is not warranted and has initiated work on a program to evaluate candidate procedures to replace the neutral buffered potassium iodide procedure.

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EVALUATION OF 1 PERCENT NEUTRAL BUFFERED POTASSIUM IODIDE PROCEDURE FOR CALIBRATION OF OZONE MONITORS

by

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SECTION 1

INTRODUCTION

In the April 30, 1971, Federal Register,[1] the Environmental Protection Agency (EPA) promulgated national ambient air quality standards for six pollutants, including a standard for photochemical oxidants (ozone). A reference method for support of that standard was described in Appendix D in that same document. The standards were subsequently codified as 40CFR Part 50, Appendix D, and amended on February 18, 1975 (FR 7042). Appendix D currently describes the measurement principle and calibration procedure. While the standard is nominally for photochemical oxidants, the reference method is specific for ozone (O_3), and is based on monitoring the chemiluminescence from the reaction of ozone and ethylene.

An O_3 generator calibrated by the 1 percent neutral buffered potassium iodide (NBKI) procedure is used to calibrate the chemiluminescence monitor. The calibration procedure is based on the reaction of one mole of O_3 with an excess of iodide (I^-) in a neutral buffered solution to produce one mole of iodine (I_2).[3] The iodine is determined colorimetrically by measuring its absorbance at 352 nm.

The NBKI procedure has been subjected to detailed study both prior to and following its promulgation as part of the reference method. Byers and Saltzman[4], and Saltzman and Gilbert[5] described the optimum use of the 1 percent NBKI method for measurement of O_3 in ambient air. Their investigations described the method much as it appears in the Federal Register and included a determination of the 1:1 O_3-I_2 stoichiometry at neutral pH. They confirmed the stoichiometry of 1:1 by conducting a gas phase titration (GPT) of O_3 with nitric oxide (NO) to produce nitrogen dioxide (NO_2) and subsequently determining the NO_2 generated.

Later, Altshuller and Wartburg[6] showed the importance of using all glass or Teflon connections in the sampling system to avoid O_3 losses. Jacobs[7] reported that impingers gave higher results than fritted glass absorbers. A challenge of the 1:1 stoichiometry of O_3:I_2 was made by Boyd et al.[8] and later refuted by Hodgeson et al.[9] and Kopczynski and Bufalini.[10] EPA and National Bureau of Standards sponsored a workshop on ozone analysis by NBKI[11] at which various researchers presented data describing their experiences with NBKI.

Despite all of these investigations, there was still considerable uncertainty within the scientific community as to the reliability of the NBKI procedure for analysis of ozone. Accordingly, the Quality Assurance Branch of the Environmental Monitoring and Support Laboratory (QAB/EMSL) developed a plan to thoroughly evaluate the NBKI procedure. This report contains the results of the evaluation.

SECTION 2

EXPERIMENTAL

A. General

The procedure used for generation and analysis of ozone used in this study is described in the Federal Register[9] with exceptions as described below. GPT procedure for calibration of NO_2 monitors is found in the June 8, 1973, Federal Register.

B. Test Atmosphere Generation

The system used to generate test atmospheres for this study are shown in Figures 1 and 2.

1. Ozone Generation

Ozone was generated continuously by ultraviolet irradiation of clean air passing through a quartz-tube. The amount of ozone produced was controlled by a movable sleeve surrounding the U-V lamp. A constant voltage transformer was used with the U-V lamp power supply to eliminate fluctuations in line voltage and, thus, assure constant output. This O_3 generator and its operating characteristics have been described in detail by Hodgeson et al.[12] and by the National Bureau of Standards.[13]

The ozone generator was calibrated for this study by GPT of National Bureau of Standards Standard Reference Material (SRM) No. 1683 (50 ppm NO in N_2) with O_3. The SRM was carefully diluted with clean air to a concentration of about 1 ppm. The exact NO concentration was calculated from flow measurements. The NO was then titrated with ozone and the decreass in the NO concentration, ΔNO, was assumed to be equivalent to the O_3 produced by the generator. A Bendix Model 8101-B Oxides of Nitrogen analyzer was used to measure the NO and NO_2 produced by the GPT system. The analyzer was modified by incorporating a Monitor Labs "Moly-Con" NO_2 converter (Monitor Labs, Inc., San Diego, Calif.). Ozone generator calibration curves were prepared by plotting sleeve settings vs O_3 generated. The generator was calibrated in this manner prior to each experiment.

NO_2 generated by the O_3-NO reaction was compared to the output of gravimetrically calibrated NO_2 permeation devices to test the validity of the calibration and the GPT system. The devices had permeation rates of 0.963 ± 0.004 µg NO_2/min and 0.668 ± 0.001 µg NO_2/min (Mean ± Standard Deviation) at 25.1 ± 0.1°C. Temperature for the devices was maintained by circulating water through a water-jacketed condensor connected to a Forma Temp, Jr. constant temperature bath. Permeation devices and their use have been described in detail.[14,15,16]

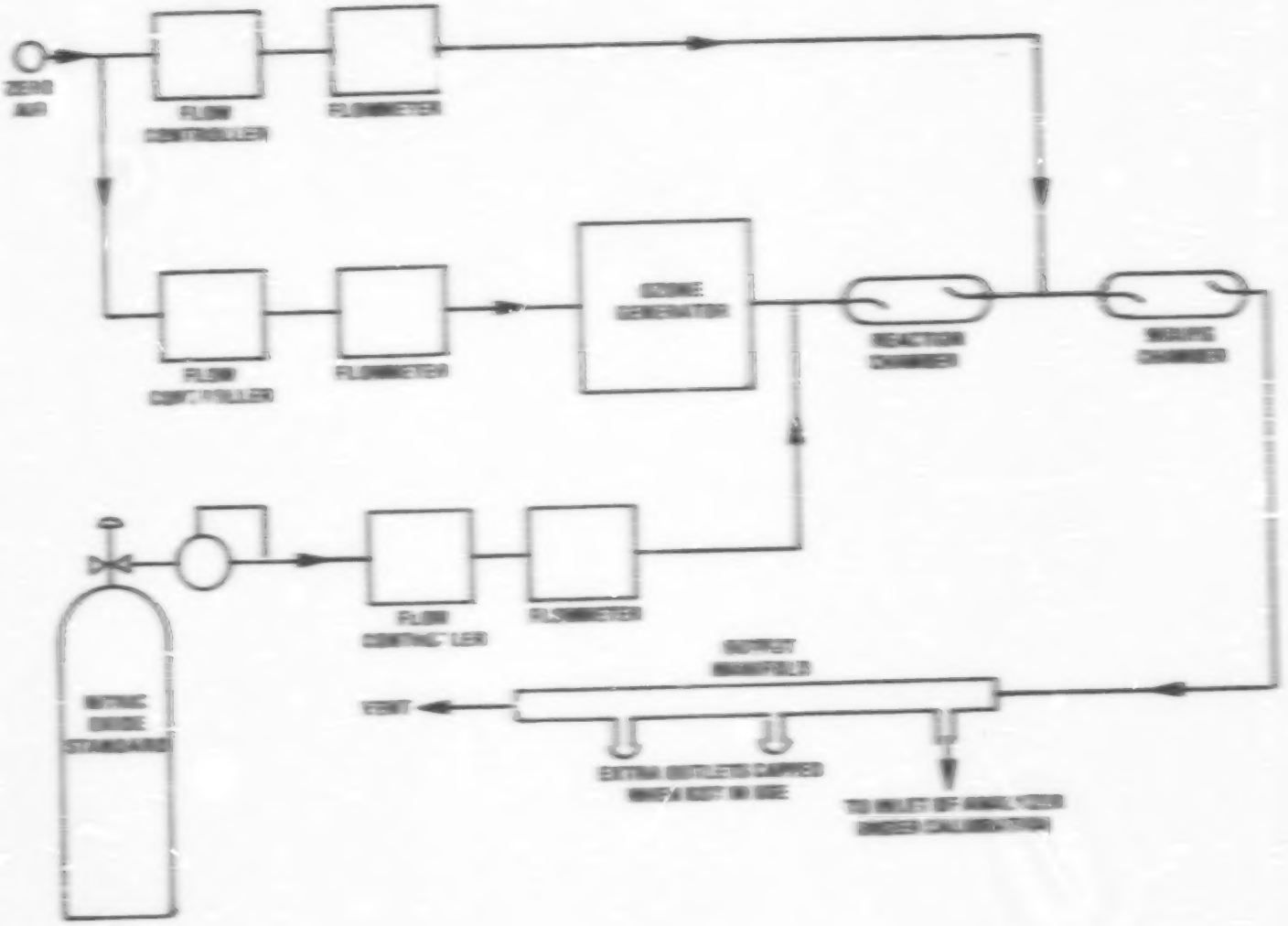

Figure 1. Schematic diagram of ozone generation system and gas phase titration apparatus.

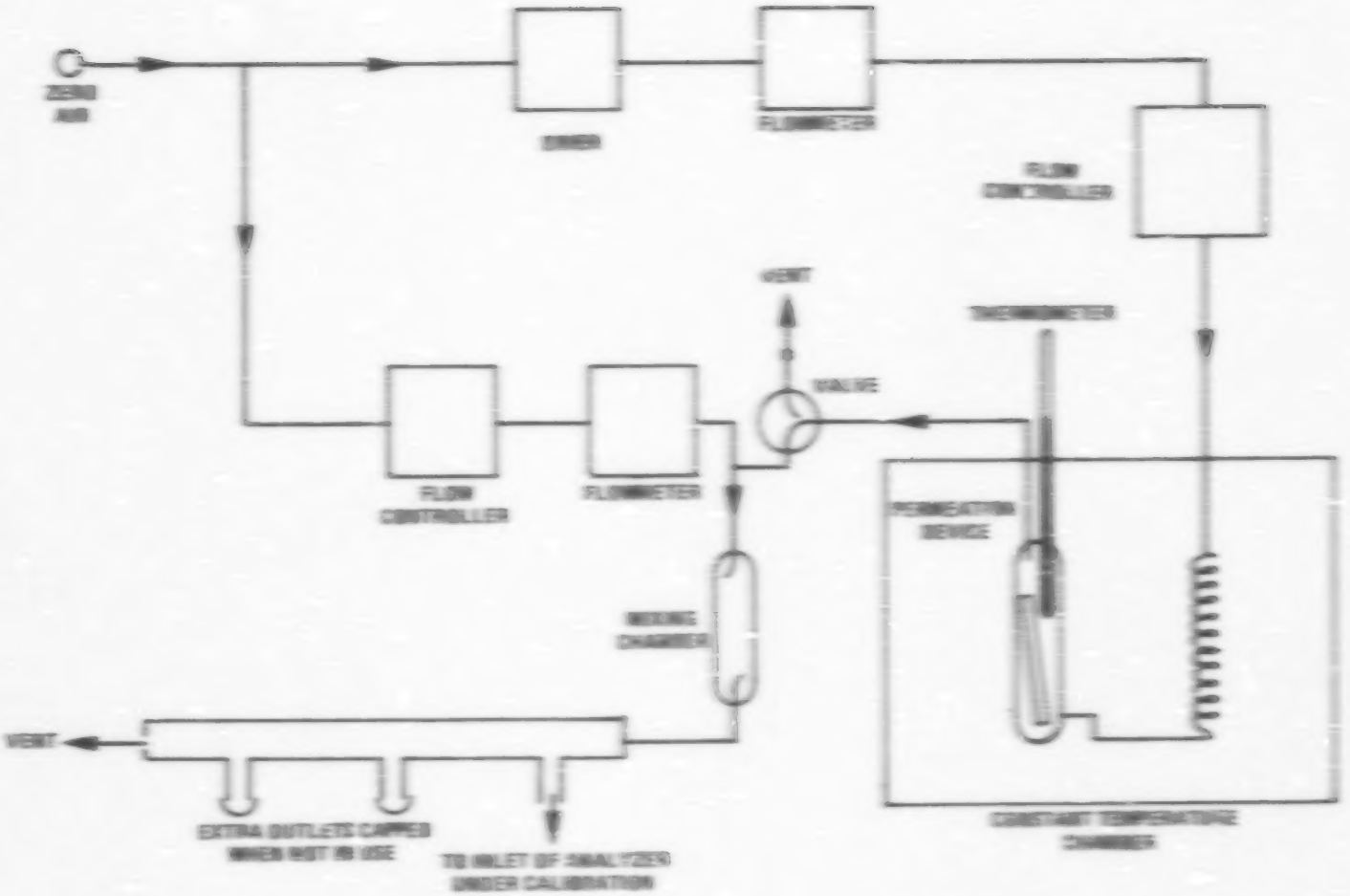

Figure 2. Schematic diagram of calibration apparatus using NO_2 permeation device

Air flow for the O_3 generator and GPT systems was effectively controlled using two single pressure regulators in series and a needle valve. NO flow from the cylinder was controlled by using a two-stage pressure regulator and a needle valve. Flow measurements were made with calibrated wet test meters and soap bubble meters.

2. Clean Air

Purified air used for O_3 generation and dilutions was produced by passing compressed (house) air through silica gel for drying, by treatment with O_3 to convert NO to NO_2, and finally by scrubbing the air with a column packed with activated charcoal (6-8 mesh), molecular sieve (8-16 mesh, type 4-A), and silica gel to remove any NO_2 or hydrocarbons and traces of water. The air was tested for completeness of NO_2 and O_3 removal by sampling with 1 percent NBKI. No background absorbance was observed.

C. Sampling and Analysis

Ozone was sampled from the output manifold, shown in Figure 1, by a train of two or more absorbers. Each absorber contained 10 ml of 1 percent NBKI. The absorbers were connected by glass tubing fitted with ground glass ball and socket connectors. All materials between the ozone sampling manifold and the absorbers were either glass or Teflon.

The iodine generated by ozone in the absorbers was analyzed by measuring its absorbance at 352 nm in a 1-cm cell. A Beckman Model "B" spectrophotometer was used for the absorbance measurements and was calibrated using iodine solutions standardized against primary standard arsenic trioxide. Absorbances were usually determined immediately (within 2 minutes after collection). However, absorbance measurements versus time were made on some samples for periods of up to 1 hour using a Varian Model 635 Spectrophotometer equipped with a strip chart recorder.

D. Test Parameters

1. Absorbers

Three types of absorbers were used for the study: 1) midget impingers (Ace Glass No. 7531), 2) modified Saltzman or "Mae West" type bubblers (Ace Glass No. 7530), and 3) a smog bubbler (Ace Glass No. 7529-16).

The absorbers were normally used in trains of two units. Some experiments employed 3-unit absorber trains to test the collection efficiency of the system.

2. Temperature

The temperature of the absorbing solution was controlled by placing the absorber in a plastic tub containing water whose temperature had been adjusted with ice or hot water to obtain working temperatures between 25 and 32°C. Absorbers and solutions were allowed to equilibrate in the bath for about 10 minutes before sampling.

3. Light Conditions

Experiments in which the absorbers were shielded from room light were conducted by covering the impingers. Normally, the absorbers were exposed to fluorescent room lighting.

4. Flow Control

Sampling flow rate was varied by the appropriate gage hypodermic needle (used as a limiting orifice to control flow in the method). When needles were not available for the desired flow, a larger needle was crimped slightly with pliers until the desired flow was obtained. The needle was protected by a membrane filter and by a drying column following the last absorber in the sampling train to ensure constant flow. All flows were measured in-train with wet test meters and soap bubble meters. Rotameters were used as flow monitoring devices.

SECTION 3

RESULTS AND DISCUSSIONS

A. Ozone Generator Calibrations

In evaluating the NBKI calibration procedure, it was imperative that the source of ozone test atmospheres be analyzed by a procedure based on accurate standards independent of the NBKI method.

A GPT method referenced to an NBS SRM NO cylinder was used to analyze the ozone atmospheres. This analysis was verified by comparison of the NO_2 generated by GPT to NO_2 generated independently with an SRM NO_2 permeation device.

The ozone generator was calibrated as described in Section 2.B.1. Four different ozone concentrations covering a range of 0.07 to 0.7 ppm were generated using sleeve settings of 10, 30, 50, and 70, and an air flow of 5 liters per minute (l/min). The calibration was performed 10 times throughout the study. The data were subjected to least squares regression analysis. A typical calibration curve for the ozone generator is shown in Figure 3 along with the equation (parabolic) for the curve. Since it has been reported by NBS,[13] and confirmed by our data, that the output of these generators is significantly nonlinear from sleeve settings of 0 to 10, the zero concentration-zero sleeve setting points were not used in the regression analysis.

Table 1 compares the mean ozone concentrations with those predicted by the parabolic regression curve derived from the GPT data. Table 1 also shows the ozone concentration that would be predicted if the nonlinearity of the generator output were ignored, i.e., fitting the data to a linear curve. At 0.07 ppm the concentration would be in error by 13 percent for this generator. At a predicted concentration of 0.05 ppm O_3, an actual concentration of 0.04 ppm was measured — an error of 20 percent! Thus, users of ozone generators should not assume the output to be linear, otherwise substantial errors may be introduced at low (near ambient) concentrations.

The NO_2 generated by the GPT of the NBS SRM NO cylinder was compared to the output of a gravimetrically calibrated NO_2 permeation device as an independent check on the accuracy of the NO SRM. The data in Table 2 show the results of that comparison. The least squares linear regression for the data is

$$[NO_2]_{GPT} = 1.012\ [NO_2]_{P.D.} + 0.0050$$

where:

$[NO_2]_{GPT}$ = NO_2 generated by GPT of NBS SRM NO cylinder

$[NO_2]_{P.D.}$ = NO_2 generated from permeation device

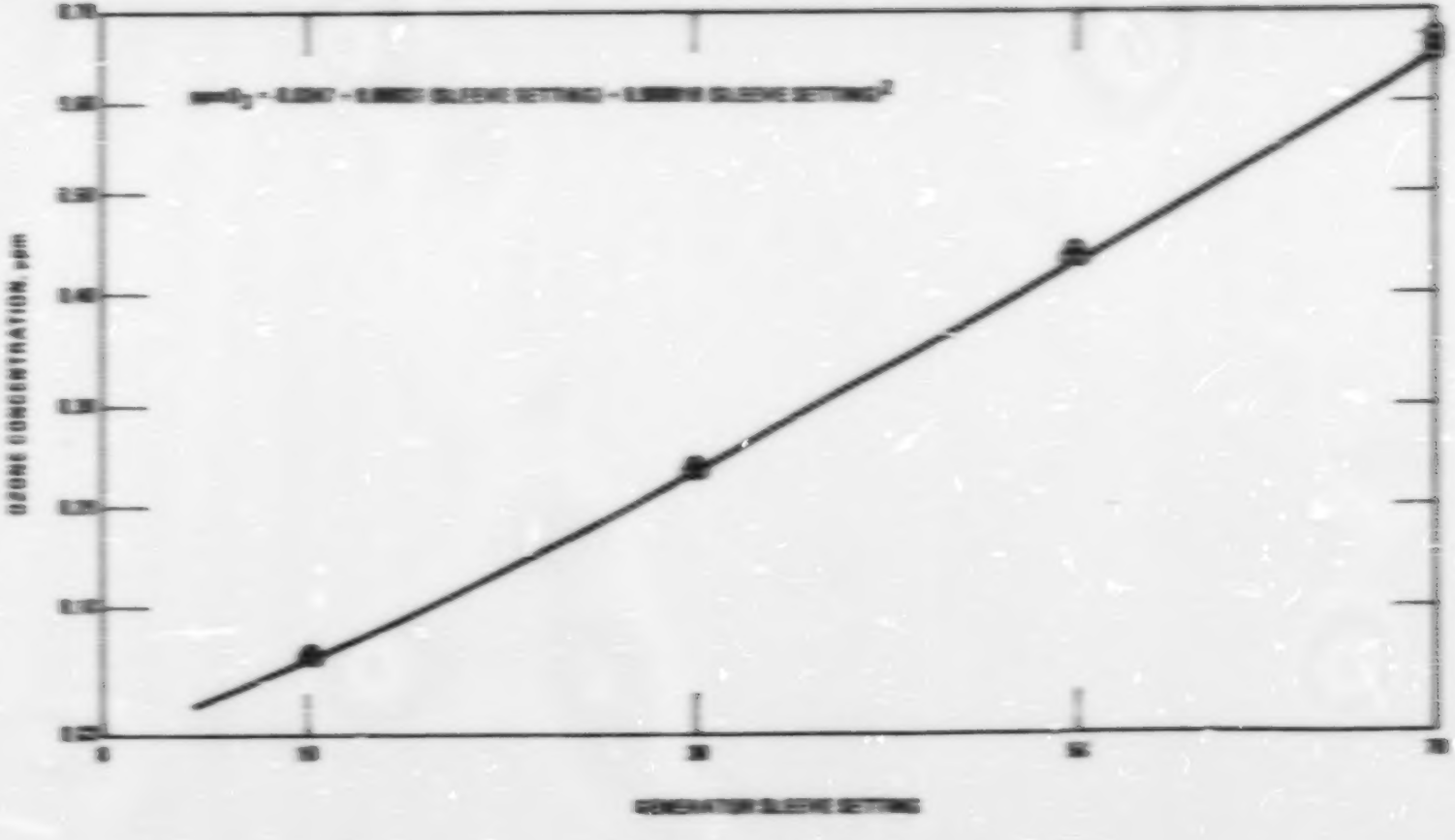

Figure 3. Calibration curve for ozone generator.

TABLE 1. COMPARISON OF MEASURED OZONE CONCENTRATION AND OZONE CONCENTRATIONS PREDICTED BY LEAST SQUARE LINEAR AND PARABOLIC REGRESSIONS (COMPOSITED DATA)

Sleeve Setting	Measured Ozone, ppm (Mean)	Predicted Ozone, ppm	
		LSLR[a]	LSPR[b]
10	0.072	0.062	0.070
30	0.267	0.277	0.271
50	0.490	0.491	0.486
70	0.714	0.705	0.715

[a]Least squares linear regression.

[b]Least squares parabolic regression.

TABLE 2. COMPARISON OF NO_2 GENERATED BY GPT OF NBS SRM NO CYLINDER AND NO_2 FROM A PERMEATION DEVICE

NO_2 Concentration, ppm	
SRM NO	Permeation Device
0.721	0.716
0.511	0.495
0.291	0.270
0.076	0.075
0.000	0.000

The slope of 1.012 is not significantly different from 1.0 at the 95 percent confidence interval. This agreement of two independent standards was considered adequate. Accordingly, the GPT calibration technique and a calibration curve like that in Figure 3 were used to obtain known ozone concentrations.

B. Evaluation Procedures

The NBKI procedure was evaluated by two methods. First, ruggedness tests as described by Youden[19] were used to screen the method for sensitive variables. Variables showing significant variation in the ruggedness tests, as well as those variables not lending themselves to ruggedness testing, were tested individually.

1. Ruggedness Testing

One requisite for a meaningful ruggedness test is that the variables have no interaction. Inclusion of a system blank or "dummy" variable in the test serves as a means of indicating whether or not the test is in control.[19] A low value obtained for the dummy variable indicates no significant interaction and means all variables are in control, whereas a high dummy value indicates interaction. The response obtained in each ruggedness test is expressed in percent recovery and was calculated by dividing the ozone concentration analyzed by the NBKI method by the ozone concentration generated. Normalization of the results was necessary before the effect of the different parameters could be determined because the method is obviously sensitive to ozone concentration.

The first ruggedness test was designed with only concentration as a variable and the remaining six variables as dummies. Ozone concentrations of 0.043 to 0.772 ppm were generated to cover a wide range of calibration concentrations. The results are given in Table 3 and show that the dummies are all low and similar. The average dummy value was 0.7 ± 0.5 percent (one standard deviation) and was used to provide a gauge for judging control in future ruggedness tests. An effect due to concentration (-5.4 percent) was observed in this test. No reason for the concentration effect was apparent at this time.

The second ruggedness test examined the effect of absorbing solution temperature and exposure of the solution to light during sample collection at ozone concentrations of 0.10 and 0.70 ppm. The four remaining variables were dummies. The absorbing solution temperature was varied 5°C to approximate the normal variation in laboratory temperature that might be experienced by users of the method.

The results in Table 4 show that the dummies are low (2.3 ± 1.3 percent, one s.d.). The responses due to temperature and light exposure were both insignificant, indicating that these variables were not affecting the method response. Again, an effect due to concentration was observed (+8.9 percent). Thus, the first two ruggedness tests suggest that ozone concentration affects the NBKI method and a separate test is in order.

The third ruggedness test examined the effect of five variables: sampling time, sampling flow rate, impinger (absorber) type, number of impingers,

TABLE 3. RUGGEDNESS TEST NO. 1

Variable	Range	Response, percent
1. Concentration, ppm	0.043 vs 0.772	-5.4
2. Dummy 1	"	-1.0
3. Dummy 2	"	+0.4
4. Dummy 3	"	-0.4
5. Dummy 4	"	+0.9
6. Dummy 5	"	-0.2
7. Dummy 6	"	+1.5

TABLE 4. RUGGEDNESS TEST NO. 2

Variable	Range[a]	Response, percent
1. Concentration, ppm	0.10 vs 0.70	+8.9
2. Collection Temp., °C	27 vs 32	+1.0
3. Light Exposure	Light vs Dark	-0.1
4. Dummy 1	"	-2.1
5. Dummy 2	"	-2.5
6. Dummy 3	"	0.7
7. Dummy 4	"	3.9

[a] The nominal variable is listed first followed by the challenging variable.

and delay time for determining absorbance. The ozone concentrations were again set at 0.10 and 0.70 ppm. One dummy variable was included in the design.

The NBKI procedure allows a sample flow rate of 0.2 to 1.0 ℓ/min and a sampling time of 10 minutes. Sampling flow rates of 0.6 and 1.0 ℓ/min and sampling time of 10 and 15 minutes were chosen to detect any differences in collection efficiency.

The use of midget impingers and modified Saltzman bubblers was compared. The modified Saltzman bubbler is specified in the method; however, experience has shown that a number of analysts use midget impingers. The number of impingers was also varied by using three instead of the specified two to see if any ozone was passing through the train of two impingers. The time allowed for measurement of iodine absorbance was also included as a variable. The method specifies that the absorbance be measured "immediately" after sample collection. The nominal and challenging variables were set at 2 and 10 minutes, respectively.

The results in Table 5 show that the response due to number of impingers and flow rate variation were low and similar to the dummy value of 3.6 percent. The most significant effect was due to the elapsed time before determination of iodine absorbance as shown by the 14.6 percent increase in response (a negative value indicates an increase in response and a positive value a decreased response). The use of the modified Saltzman impinger appears to reduce the method's response relative to the midget impinger. Increasing the sampling time from 10 to 15 minutes increased the response by 6 percent.

The fourth ruggedness test (Table 6) again used ozone concentrations of 0.10 and 0.70 ppm and one dummy variable. The high dummy value of 16.5 percent and high responses for nearly all the variables suggested that considerable interaction between variables was occurring.

Reviewing the foregoing ruggedness tests showed that as the number of variables increased, the dummy values also increased. Also, Ruggedness Test 2 showed a negligible effect (-0.1 percent) for light vs. dark sampling conditions where Test No. 4 showed an appreciable effect (-14.3 percent) for the same variable. Similar worsening effects were seen for other variables.

The occurrence of interactions and varying results in the ruggedness tests emphasize the need to strictly follow the procedure. Apparent modest changes in the procedure, as introduced in the fourth ruggedness test, produced highly variable results.

Further investigation of the NBKI method was conducted through individual tests of sensitive variables identified by the ruggedness tests as well as tests on previously examined variables.

2. Single Variable Experiments

a. Absorption Maximum of I_2

The absorption spectrum of a 1 percent NBKI solution containing I_2 (generated by O_3 was determined by scanning in the 350-nm region (using a Varian Model 635 Spectrophotometer). The scan confirmed the reported absorbance maximum of I_2 at 352 nm.[1,3,4]

TABLE 6. RUGGEDNESS TEST NO. 3

Variables	Range[a]	Response, percent
1. Concentration, ppm	0.10 vs 0.20	+6.4
2. Absorbance Det., min	2 vs 10	-14.6
3. Impinger Type	Midget vs Modified Saltzman	+6.6
4. No. of Impingers	2 vs 3	+3.0
5. Sampling Time, min	10 vs 15	-6.2
6. Sampling Rate, l/min	0.6 vs 1.0	-4.6
7. Dummy	-	-3.6

[a] The nominal variable is listed first followed by the challenging variable.

TABLE 6. RUGGEDNESS TEST NO. 4

Variable	Range[a]	Response, percent
1. Impinger Type	Midget vs Smog Bubbler	23.8
2. Buffer Reagent	$KH_2PO_4 \cdot 7H_2O$ vs Anhydrous KH_2PO_4	19.1
3. Dummy	-	-16.5
4. Concentration, ppm	0.10 vs 0.70	15.5
5. Light Exposure	Light vs Dark	-14.3
6. Sampling Rate, l/min	1.0 vs 1.5	13.5
7. Collection Temp., °C	25 vs 30	-6.2

[a]The nominal variable is listed first followed by the challenging variable.

b. Absorbance Development Time

Prior to determining the effect of time on the development of iodine absorbance, the stability of the iodine standards used for spectrophotometer calibration (in the method) was determined. The absorbance was read immediately (2 minutes) after individual preparation, and again after 30 minutes and 2 hours. All standards were in Pyrex volumetric flasks and were capped with ground glass stoppers. The data in Table 7 show no significant change in absorbance. According to Clements,[10] data reported by Hodgeson for a similar experiment showed a decrease in absorbance with time. However, a verbal communication with Dr. Hodgeson revealed that his flasks were not stoppered during his experiments. This observation points out the importance of eliminating possible losses of iodine by volatilization or reaction with air.

The absorbance of iodine with time, generated by sampling four concentrations of ozone, is shown in Figure 4. These data show an increase in absorbance with time; at concentrations above 0.1 ppm, maximum color development occurs in about 40 to 50 minutes. The absorbance increase is about 6 to 8 percent except at the lowest concentration, for which the absorbance is constant. These data are similar to data reported by Saltzman and Gilbert[7] who postulated several mechanisms to account for the increased absorbance. Since the method calls for "immediate" determination of the sample absorbance, one might think that this increase should not be a factor. However, due to the variation of apparatus and technique from one analyst to another, appreciable differences might be observed.

c. Effect of Type of Absorber

The effect of different types of absorbers was investigated further by sampling common atmospheres, over the range 0.2 to 1.0 ppm, with two modified Saltzman bubblers and two midget impingers. The ozone concentration was then determined using the NBKI analysis procedure. The data are given in Table 8. The least square linear regression equation for this data is ppm $O_{3(Mid. Imp.)}$ = 1.164 ppm $O_{3(Mod. Saltzman)}$ - 0.030. Thus, midget impingers collect about 16 percent more ozone than Modified Saltzman bubblers. This finding is in good agreement with the results of similar experiments carried out at 0.2 ppm ozone.[10] It is assumed that the difference is due to losses in the Modified Saltzman bubbler. The data in Table 8 also show that the increased efficiency of the midget impinger results from increased absorbance in the first impinger only.

A smog bubbler similar to the modified Saltzman bubbler having a deeper collection chamber and a 1-mm capillary orifice (Ace Glass No. 7529-16) was also compared to the midget impinger. Both of these factors should increase the O_3-KI contact time and possibly improve the collection efficiency. However, the smog bubbler gave low results similar to those of the modified Saltzman bubbler. The reason for the higher efficiency of the midget impinger over the bubbler is possibly related to differences in surface area and volume.

d. Purity of Potassium Iodide

It has been reported that certain lots of ACS Reagent Grade Potassium Iodide contain small amounts of an impurity that exhibits an iodine (ozone) demand.[20] The iodine demand was confirmed in this study and is demonstrated in the iodine vs absorbance calibration curve in Figure 5. The KI used in this test has an iodine

TABLE 7. STABILITY OF PREPARED IODINE STANDARDS WITH TIME

	Absorbance at 352 nm		
Concentration[a]	2 min	30 min	2 hr
0.975	0.058	0.055	0.059
2.44	0.133	0.130	-
4.88	0.262	0.259	0.262
9.76	0.524	0.521	0.518
14.6	0.782	0.779	-
19.5	1.035	1.032	1.023

[a]Iodine concentrations expressed as $\mu g\ O_3$.

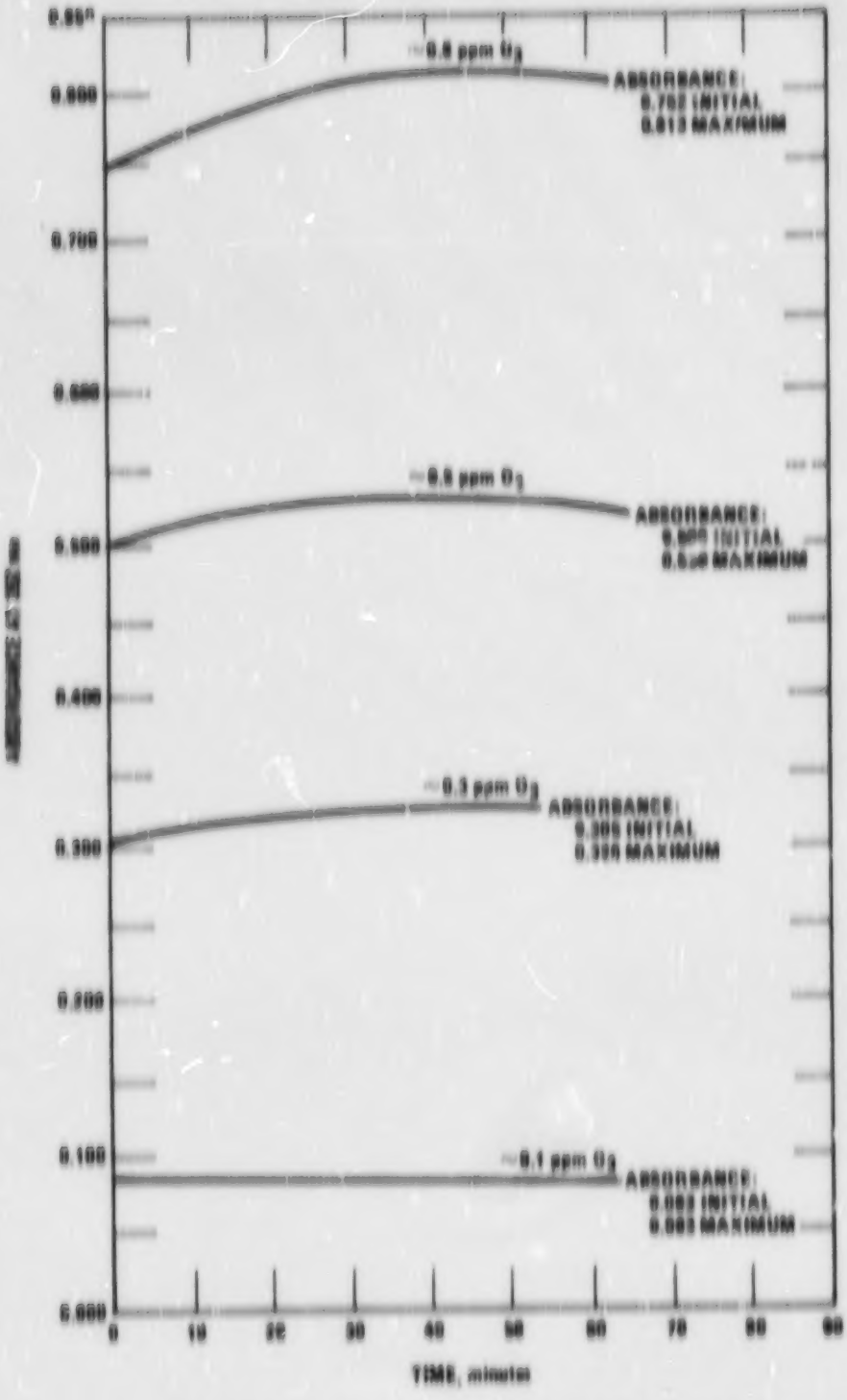

Figure 4. Absorbance of I_2 equivalent to O_3 versus time.

TABLE 8. OZONE RECOVERY FROM MIDGET IMPINGERS VS MODIFIED SALTZMAN BUBBLERS

Midget Impingers	Absorbance			
	No. 1	No. 2	Total Abs	O_3 Concentration, ppm
	0.142	0.014	0.156	0.183
	0.318	0.025	0.343	0.399
	0.495	0.037	0.565	0.618
	0.798	0.061	0.859	0.996

Modified Saltzman	Absorbance			
	No. 1	No. 2	Total Abs	O_3 Concentration, ppm
	0.141	0.012	0.153	0.179
	0.289	0.025	0.314	0.366
	0.454	0.035	0.489	0.568
	0.696	0.058	0.754	0.875

demand equivalent to 0.83 ug O_3, as indicated by the large positive intercept of the least squares linear regression equation. This amount of ozone is equivalent to 0.05 ppm O_3 at a sampling rate of 1.0 l/min and a 10-minute sampling time.

A different lot of ACS reagent grade KI was used to obtain the calibration curve shown in Figure 6. Here the intercept is only 0.01. A review of several similar calibration curves showed a slope of 19.22 ± 0.45 ug O_3/Abs (Mean ± 95 percent confidence band) and an average intercept of -0.06 ± 0.74 ug O_3 (Mean ± 95 percent confidence band). Thus, KI of acceptable purity should yield an intercept in the range -0.20 to +0.08 95 percent of the time. If in preparing a calibration curve an analyst obtains an intercept outside of this range, the KI should be rejected and a new lot of KI should be used to prepare another calibration curve.

e. One Percent NBKI Stability

The effect of (1) storage in different types of containers, (2) exposure to room light and temperature, and (3) exposure to elevated temperature on the absorbance of the 1 percent NBKI reagent and its ability to collect ozone was tested. The containers were as follows:

B. Blank (reference) low actinic flask

1. Clear Lurex 500-ml volumetric flask
2. Low actinic 500-ml Pyrex flask
3. Clear Pyrex reagent bottle
4. Dark brown Pyrex reagent bottle
5. Clear glass reagent bottle
6. Dark brown glass reagent bottle
7. Teflon bottle
8. Clear Nalgene bottle
9. Dark brown Nalgene bottle

The containers were washed with cleaning acid, rinsed thoroughly with distilled water, and rinsed and then filled with freshly prepared 1 percent NBKI. They were then placed on the laboratory counter where they were exposed to existing conditions of light and temperature. A reagent blank "B" was stored in the dark for use as a reference.

Stability was measured by comparing the absorbance of the different solutions with the blank value over an 8-week period and by using the same solutions (and the blank) to sample an atmosphere containing 0.10 ppm ozone seven times over the same time period. No significant change in absorbance or ability to collect ozone was observed over the 8-week test period.

Portions of the solutions exposed to room conditions from containers 1, 2, 8 and 9 and the blank were then heated to 38°C (from 25°C) and held at this temperature for 6 hours. The solutions were then cooled to 25°C, their absorbance was compared to the unheated blank, and they were used to sample the 0.10-ppm ozone atmosphere, as in the previous experiments. The solutions subjected to temperature cycling showed a decrease in their absorbance background, but no loss in their ability to collect ozone when referenced to the blank sample that had been heated to 38°C also.

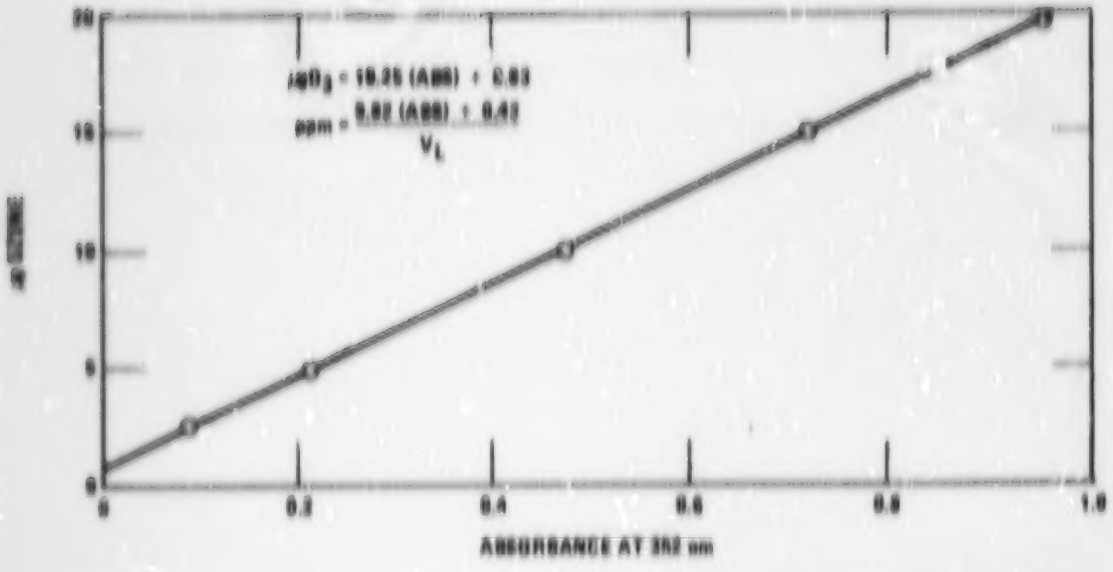

Figure 5. I_2 versus absorbance calibration with impure ACS reagent grade potassium iodide.

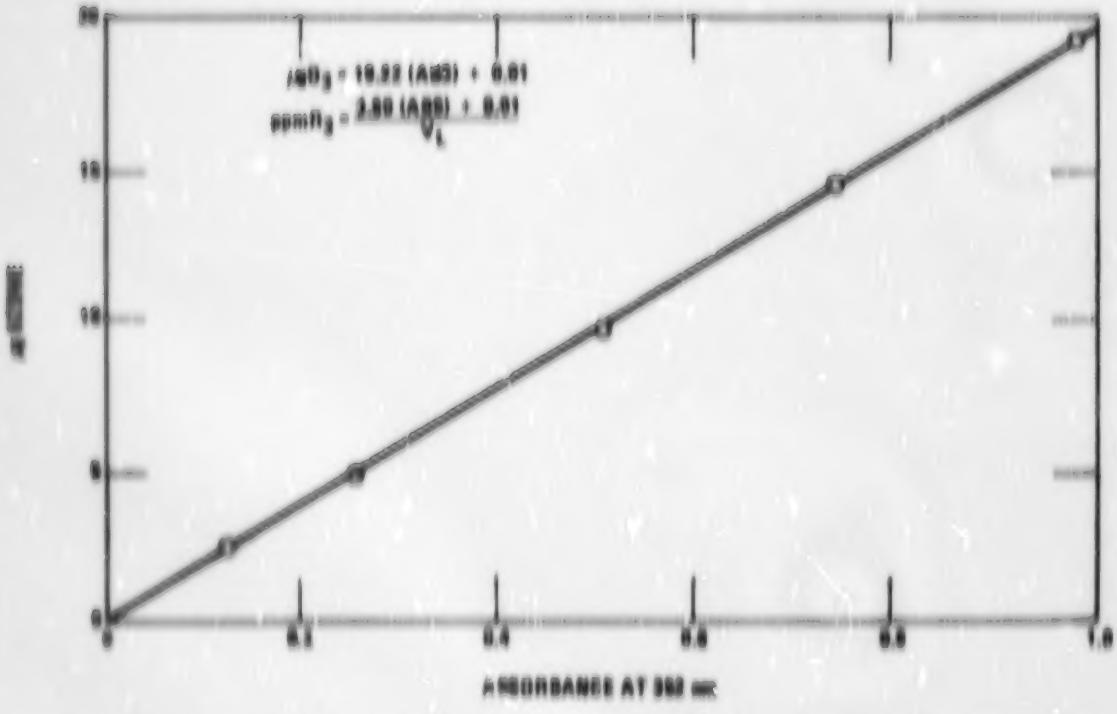

Figure 6. I_2 versus absorbance calibration with "pure" ACS reagent grade potassium iodide.

From these experiments it is concluded that the stability of the 1 percent NBKI reagent does not appear to be an important variable.

C. Improvements in the Published NBKI Calibration Procedure

Based on the findings of this study, a document was prepared which gives the essential details for an improved NBKI procedure. The document is given in the Appendix. The main points are (a) use of a constant voltage transformer with the ozone generator to ensure the constancy of the ozone being sampled, (b) use of midget impingers instead of modified Saltzman bubblers, (c) specifications and a procedure for determining KI purity, and (d) stressing the importance of measuring the iodine absorbance within three minutes. The errors associated with the method should be reduced if one follows the instructions and clarifications in this document.

D. Comparison of Improved Procedure with GPT

The improved NBKI procedure was used to analyze ozone atmospheres generated by a GPT-calibrated ozone generator over the range 0.07 to 0.72 ppm. The results are shown in Figure 7. The regression equation slope is

$$O_{3NBKI} = 1.075(O_{GPT}) \pm 0.034 \text{ (95\% C.I.)}$$

These data indicate an average positive bias in the NBKI procedure of 7.5 percent with a range of 4 to 11 percent. This result compares favorably with similar experiments reported by Paur et al.,[20] which showed slopes from 1.0 to 1.11.

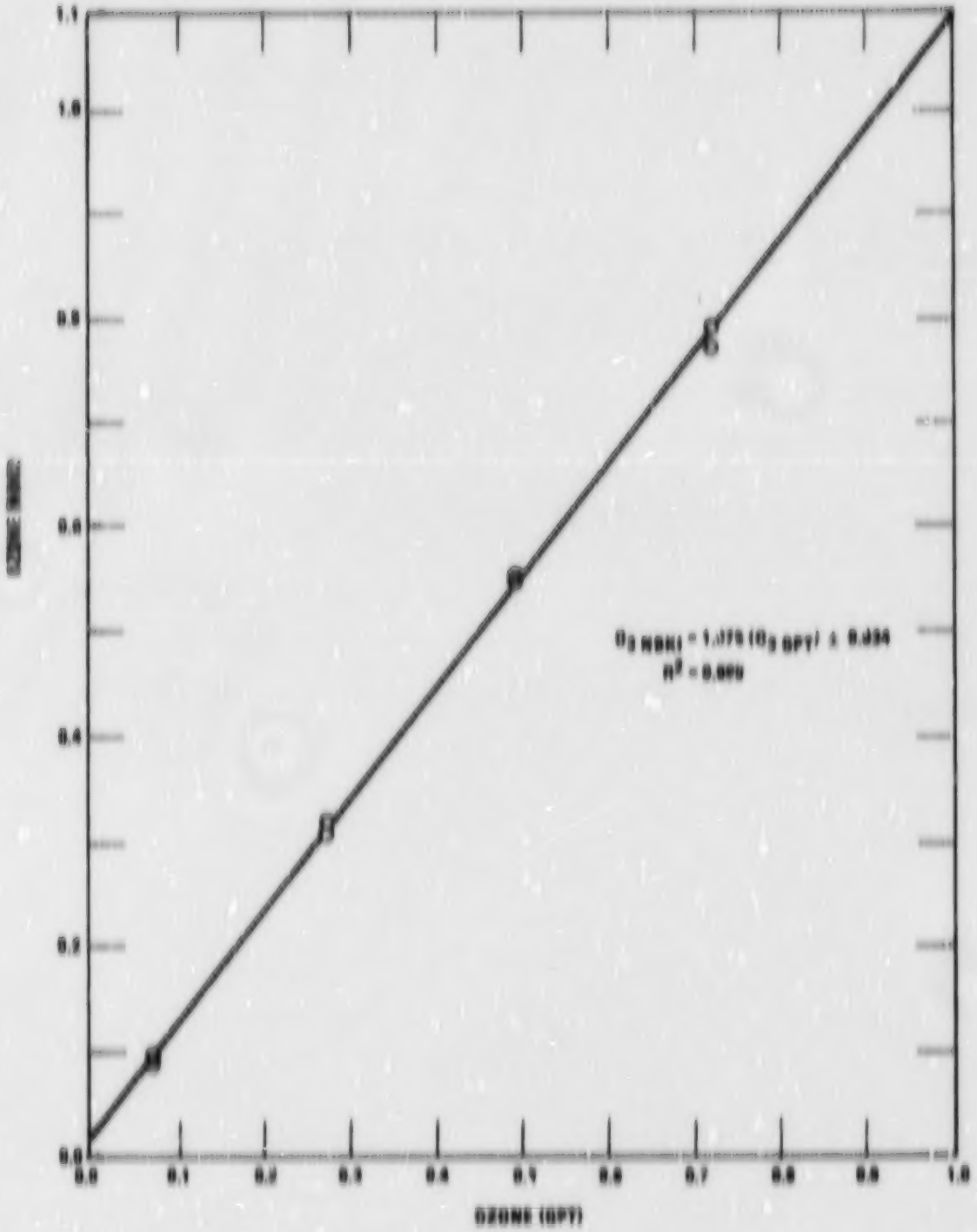

Figure 7. Comparison of neutral buffered potassium iodide method for ozone with gas phase titration chemiluminescence method.

SECTION 4

CONCLUSIONS

The results of this study show that the NBKI procedure is vulnerable to error in three major areas: 1) the time allowed for measurement of iodine absorbance, 2) purity of potassium iodide reagent, and 3) type of impinger used. The reasons for some of these errors are not fully understood and, therefore, are difficult to control. Erratic results brought about by modest changes in operating procedure, such as those introduced in the ruggedness tests, suggest that widely varying results may be obtained in actual use.

Under ideal use conditions, the NBKI procedure has a small but significant positive bias.

Since calibration procedures that appear more promising than NBKI are now available (gas phase titration and UV-photometry), OAB/EMSL has decided that further work on improving the current NBKI procedure is not warranted. A verbal communication with Dr. Daniel Flamm of Texas A&M University indicates an alternate iodometric procedure may be developed to overcome some of the problems with the NBKI procedure. Accordingly, a program has been initiated to evaluate the above procedures as candidates to replace the NBKI procedure. In the interim period, the NBKI procedure should be used as specified in the clarification memorandum to improve data quality.

SECTION 5

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APPENDIX A

APPENDIX A: TECHNICAL GUIDANCE FOR OBTAINING IMPROVED PRECISION AND ACCURACY IN USING THE OZONE CALIBRATION PROCEDURE GIVEN IN 40 CFR PART 50, APPENDIX D.

The reference method calibration procedure specified in Appendix D of 40 CFR Part 50 allows a moderate degree of flexibility in a number of its provisions. This flexibility arises because some of the equipment and procedural specifications are given in terms which tend to be general or subject to interpretation, rather than highly specific. Such general-type specifications permit variations to accomodate operator preferences and available equipment. However these variations compromise, to some extent, the precision and accuracy of the resulting ozone measurements.

Within certain somewhat general specifications prescribed in Appendix D of 40 CFR Part 50, it is possible to obtain improved precision and accuracy by following more detailed and restrictive procedures. These augmentative procedures and instructions are set forth below for those who wish to obtain improved results. While use of these additional instructions is not required, EPA recommends that they be followed where improved uniformity and accuracy are desired.

1. Section 5.10.1 indicates that "all-glass impingers as shown in Figure D4 are recommended". It is obvious that the intent of this specification is not to exclusively limit the type of absorber used to the exact type or shape shown in Figure D4. A number of other all-glass absorbers are available and are permissable under the intent of section 5.10.1. EPA now believes that the best uniformity and accuracy are obtained by the use of a type of absorber referred to as a "midget impinger". Specifications for this midget impinger are given in Figure 1.

2. Section 6 indicates the reagents which are required to carry out the procedure. Greater uniformity and accuracy may be obtained if the following reagents are specified as "ACS Reagent Grade": potassium iodide (KI), potassium dihydrogen phosphate (KH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), sodium hydroxide (NaOH), sulfuric acid 95% to 98% (H_2SO_4), starch (soluble), mercuric iodide (HgI_2), iodine (resublimed I_2), and sodium bicarbonate ($NaHCO_3$).

3. Section 6.5 specifies the use of either anhydrous disodium hydrogen phosphate (Na_2HOP_4) or the dodecahydrate salt ($Na_2HOP_4 \cdot 12H_2O$). However the heptahydrate form of this compound ($Na_2HOP_4 \cdot 7H_2O$) is more stable and this provides improved precision. Since all three of these forms of the compound are absolutely equivalent chemically, the heptahydrate form is recommended. The equivalent quantity of $Na_2HOP_4 \cdot 7H_2O$ is 26.8 grams.

4. Section 6.5 specifies the use of potassium iodide (KI). Some sources of KI -- even ACS Reagent Grade -- have been reported to contain small amounts of reducing agents. Such impurities can cause an iodine demand which could cause a significant measurement error. Best accuracy is thus obtained with KI which has no significant iodine demand. To determine if this specification is being met, plot the I_2 absorbance (y-axis) versus total ug O_3 (x-axis) calibration curve in section 6.1.2 as follows:

> Plot the five points obtained for the 0.5, 1, 2, 3, and 4 ml of I_2. Do not include zero as a point. Draw the curve or use linear regression analysis. If the intercept is significantly different from zero, the KI has an I_2 demand and should be discarded. Typical intercepts obtained at NERC/RTP are between +0.08 and -0.20 ug O_3. Typical slopes obtained for the I_2 vs Absorbance are between 19.67 and 18.77 ug O_3/Absorbance Unit.

5. Section 6.2 specifies "cylinder air, dry grade". This specification is rather ambiguous, but it seems clear that the intent is to require air of a clean, dry, and uniform quality. Air from sources other than compressed gas cylinders can certainly meet and exceed those requirements. Thus, this specification can be interpreted to include any source of clean, dry, uniform air. But again, greater precision can be realized if additional specifications are applied to the air. In particular, the air must also be essentially free of ozone, NO, NO_2, reactive hydrocarbons, and any other interferent which may cause a positive or negative bias. While it is not practical to attempt to analyze the air for presence of these various interferents, air meeting the above additional requirements may be produced by appropriate treatment as described below. Either compressed ambient air or cylinder air may be treated. The air is first passed through silica gel for drying, then it is treated with ozone to convert any NO to NO_2. Finally, the air is passed through 6-14 mesh activated carbon and 6-16 mesh type 4A molecular sieve to remove NO_2 and hydrocarbons.

> NOTE: The oxygen content of cylinder air may vary from 18% to 22%, which can cause changes in the calibration of ozone generators. If cylinder air is used, recalibration of the ozone generator with each new cylinder of air is recommended.

6. Sections 8.1.1, 8.2.2.1, and 8.2.2.2 all require measurement of the iodine absorbance "immediately". Best precision is obtained when these measurements are made within 3 minutes after obtaining the material to be measured.

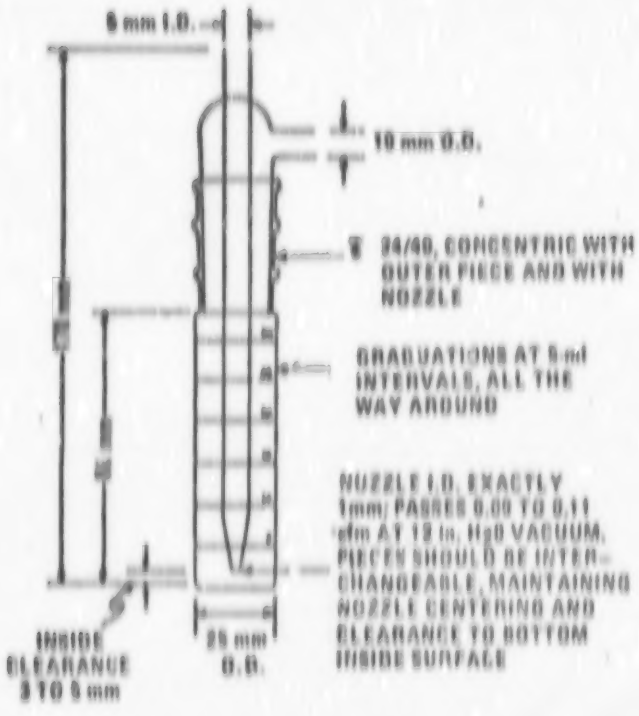
5 mm I.D.
10 mm O.D.
24/40, CONCENTRIC WITH OUTER PIECE AND WITH NOZZLE
GRADUATIONS AT 5 ml INTERVALS, ALL THE WAY AROUND
NUZZLE I.D. EXACTLY 1mm; PASSES 0.09 TO 0.11 cfm AT 12 in. H_2O VACUUM. PIECES SHOULD BE INTER-CHANGEABLE, MAINTAINING NOZZLE CENTERING AND CLEARANCE TO BOTTOM INSIDE SURFACE
INSIDE CLEARANCE 3 TO 5 mm
25 mm O.D.

Figure 1.

APPENDIX B

code of federal regulations

40

Protection of Environment

PARTS 50 TO 69

Revised as of July 1, 1979

CONTAINING
A CODIFICATION OF DOCUMENTS
OF GENERAL APPLICABILITY
AND FUTURE EFFECT

AS OF JULY 1, 1979

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Appendix C—Measurement Principle and Calibration Procedure for the Continuous Measurement of Carbon Monoxide in the Atmosphere (Non-Dispersive Infrared Spectrometry)

1. *Principle and applicability.*

1.1 The principle is based on the absorption of infrared radiation by carbon monoxide in a non-dispersive photometer. Both beams pass into matched cells, each containing a detector and CO. The CO in the cells absorb infrared radiation only at the characteristic frequencies and the detector is sensitive to these frequencies. With a non-absorbing gas in the reference cell, and with no CO in the sample cell, the signals from both detectors are balanced electronically. Any CO introduced into the sample cell will absorb radiation, which reduces the temperature and pressure in the detector cell and displaces a diaphragm. This displacement is detected electronically and amplified to provide an output signal.

1.2 An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Part 53 of this chapter.

2. [Reserved]

3. *Procedure.*

3.1 Calibrate the instrument as described in 5.1. All gases (sample, zero, calibration, and span) must be introduced into the entire analyzer system. Figure 1 shows a representative diagram. For specific operating instructions, refer to the manufacturer's manual.

4. *Calibration.*

4.1 *Calibration Curve.* Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value on the recorder. Use 100 ppm or 0.50 mg/m³ scale; set the 10 mg/m³ standard at 80 percent of the recorder chart. Recheck zero and span. Adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a uniform curve is not obtained, calibration gases may need replacement.

5. *Calculations.*

5.1 Determine the concentrations directly from the calibration curve. No calculations are necessary.

5.2 Carbon monoxide concentrations in mg/m³ are converted to p.p.m. as follows:

$$\text{p.p.m. CO} = \text{mg. CO/m}^3 \times 0.873$$

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[36 FR 22384, Nov. 25, 1971, as amended at 40 FR 7044, Feb. 18, 1975]

Appendix D—Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Ultraviolet Photometry)

1. *Principle and applicability.*

1.1 Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

1.2 An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with Part 53 of this chapter.

2. [Reserved]

3. *Apparatus.*

3.1–3.9 [Reserved]

3.10 *Apparatus for Calibration.*

3.10.1 *Absorber.* All-glass impingers as shown in Figure D4 are recommended. The impingers may be purchased from most laboratory glassware suppliers. Two absorbers in series are needed to ensure complete collection of the sample.

3.10.2 *Air Pump.* Capable of drawing 1 liter/minute through the absorbers. The pump should be equipped with a needle valve on the inlet side to regulate flow.

3.10.3 *Thermometer.* With an accuracy of ±2° C.

3.10.4 *Barometer.* Accurate to the nearest mm. Hg.

3.10.5 *Flowmeter.* Calibrated metering device for measuring flow up to 1 liter/minute within ±2 percent. (For measuring flow through impingers.)

3.10.6 *Flowmeter.* For measuring airflow past the lamp; must be capable of measuring flows from 2 to 10 liters/minute within ±2 percent.

3.10.7 *Trap.* Containing glass wool to protect needle valve.

3.10.8 *Volumetric Flasks.* 25, 100, 500, 1,000 ml.

3.10.9 *Buret.* 50 ml.

3.10.10 *Pipets.* 0.5, 1, 5, 9, 1, 10, 25, and 50 ml. volumetric.

3.10.11 *Erlenmeyer Flasks.* 500 ml.

3.10.12 *Spectrophotometer.* Capable of measuring absorbance at 352 nm. Matched 1-cm. cells should be used.

4. *Reagents.*

4.1 *Ethylene.* C. P. grade (minimum).

6.2 *Cylinder Air.* Dry grade.

6.3 *Activated Charcoal Trap.* For filtering cylinder air.

6.4 *Purified Water.* Used for all reagents. Tri-distilled or deionized water in an all-glass distillation apparatus and a crystal of potassium permanganate and a crystal of barium hydroxide, and redistill.

6.5 *Absorbing Reagent.* Dissolve 13.6 g potassium dihydrogen phosphate (KH_2PO_4), 14.2 g anhydrous disodium hydrogen phosphate (Na_2HPO_4), 1.0 g sodium hydroxide and 10.0 g potassium iodide (KI) in purified water and dilute to 1 liter. The pH should be 8.8 ± 0.5. The solution is stable for several weeks if stored in a glass-stoppered amber bottle in a cool, dark place.

6.6 *Standard Arsenious Oxide Solution (0.05 N).* Use primary standard grade arsenious oxide (As_2O_3). Dry 1 hour at 105° C. immediately before using. Accurately weigh, to the nearest 0.1 mg, 0.4 g arsenious oxide from a small glass-stoppered weighing bottle. Transfer to 25 ml 1 N sodium hydroxide in a flask or beaker on a steam bath. Add 50 ml 1 N sulfuric acid, then, transfer quantitatively to a 1,000-ml volumetric flask, and dilute to volume. Note: Solution must be neutral to litmus, not alkaline.

$$\text{Normality } As_2O_3 = \frac{\text{wt } As_2O_3 \text{ (g)}}{0.0495}$$

6.7 *Starch Indicator Solution (0.5 percent).* Triturate 0.5 g soluble starch and approximately 2 mg mercuric iodide (preservative) with a little water. Add the paste slowly to 100 ml of boiling water. Continue boiling until the solution is clear, allow to cool, and transfer to a glass-stoppered bottle.

6.8 *Standard Iodine Soln. (0.05 N).*

6.8.1 *Preparation.* Dissolve 20 g potassium iodide (KI) and 6.5 g resublimed iodine (I_2) in 10 ml purified water. When the iodine dissolves, transfer the solution to a 500-ml glass stoppered volumetric flask. Dilute to mark with purified water and mix thoroughly. Keep solution in a dark brown glass-stoppered bottle away from light, and restandardize as necessary.

6.8.2 *Standardization.* Pipet accurately 25 ml standard arsenious oxide solution into a 500-ml Erlenmeyer flask. Acidify slightly with 1:10 sulfuric acid, neutralize with solid sodium bicarbonate, and add about 2 g excess. Titrate with the standard iodine solution using 5 ml starch solution as indicator. Saturate the solution with carbon dioxide near the end point by adding 1 ml of 1:10 sulfuric acid. Continue the titration to the first appearance of a blue color which persists for 30 seconds.

$$\text{Normality } I_2 = \frac{\text{ml } As_2O_3 \times \text{Normality } As_2O_3}{\text{ml } I_2}$$

6.9 *Diluted Standard Iodine.* Immediately before use, pipet 1 ml standard iodine solution into a 100-ml volumetric flask and dilute to volume with absorbing reagent.

7. *Procedure.*

7.1 *Instruments* can be constructed from the components given here or may be purchased. If commercial instruments are used, follow the specific instructions given in the manufacturer's manual. Calibrate the instrument as directed in section 8. Introduce samples into the system under the same conditions of pressure and flow rate as are used in calibration. By proper adjustments of zero and span controls, direct reading of ozone concentration is possible.

8. *Calibration.*

8.1 *NI Calibration Curve.* Prepare a curve of absorbance of various iodine solutions against calculated ozone equivalents as follows:

8.1.1 Into a series of 25 ml volumetric flasks, pipet 0.5, 1, 2, 3, and 4 ml of diluted standard iodine solution (6.9). Dilute each to the mark with absorbing reagent. Mix thoroughly, and immediately read the absorbance of each at 352 nm, against unexposed absorbing reagent as the reference.

8.1.2 Calculate the concentration of the solutions as total μg O_3 as follows:

$$\text{Total } \mu g\ O_3 = (N_1)(48)(V_1)$$

N_1 = Normality I_2 (see 6.8.2), meq/ml.

V_1 = Volume of diluted standard I_2 added, ml. (0.5, 1, 2, 3, 4).

Plot absorbance versus total μg O_3.

8.2 *Instrument Calibration.*

8.2.1 *Generation of Test Atmospheres.* Assemble the apparatus as shown in Figure IIA. The ozone concentration produced by the generator can be varied by changing the position of the adjustable sleeve. For calibration of ambient air analyzers, the ozone source should be capable of producing ozone concentrations in the range 100 to 1,000 $\mu g/m^3$ (0.05 to 0.5 p.p.m.) at a flow rate of at least 5 liters per minute. At all times the airflow through the generator must be greater than the total flow required by the sampling systems.

8.2.2 *Sampling and Analysis of Test Atmospheres.* Assemble the NI sampling train as shown in Figure IIB. Use ground-glass connections upstream from the impinger. Butt-to-butt connections with Tygon tubing may be used. The manifold distributing the test atmosphere must be sampled simultaneously by the NI sampling train and the instrument to be calibrated. Check assembled systems for leaks. Record the instrument response in hanman-zeros at each concentration (usually six). Establish these concentrations by analysis, using the bet-

and buffered potassium iodide method as follows:

8.6.1 *Blank.* With ozone lamp off, flush the system for several minutes to remove residual ozone. Pipet 10 ml absorbing reagent into each absorber. Draw air from the ozone generating system through the sampling train at 0.5 to 1 liter/minute for 10 minutes. Immediately transfer the exposed solution to a clean 1-cm. cell. Determine the absorbance at 600 nm, against unexposed absorbing reagent as the reference. If the system blank gives an absorbance, continue flushing the ozone generation system until no absorbance is obtained.

8.6.2 *Test Atmosphere.* With the ozone lamp operating, equilibrate the system for about 10 minutes. Pipet 10 ml of absorbing reagent into each absorber and collect sample for 10 minutes in the concentration range desired for calibration. Immediately transfer the exposed solutions from the two absorbers to clean 1-cm. cells. Determine the absorbance of each at 600 nm, against unexposed absorbing reagent as the reference. Add the absorbances of the two solutions to obtain total absorbance. Read total μg O_3 from the calibration curve (see 9.1). Calculate total volume of air sampled corrected to reference conditions of 25° C. and 760 mm. Hg, as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{t + 273} \times 10^{-3}$$

V_s = Volume of air at reference conditions, m^3

V = Volume of air at sampling conditions, liters.

P = Barometric pressure at sampling conditions, mm. Hg.

t = Temperature at sampling conditions, °C.

10^{-3} = Conversion of liters to m^3

Calculate ozone concentration in p.p.m. as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{V_s} \times 5.10 \times 10^{-4}$$

8.6.3 *Instrument Calibration Curve.* Instrument response from the photomultiplier tube is ordinarily in current or voltage. Plot the current, or voltage if appropriate, (y-axis) for the test atmosphere against ozone concentration as determined by the neutral buffered potassium iodide method, in p.p.m. (x-axis).

9 *Calculations.*

9.1 If a recorder is used which has been properly zeroed and spanned, ozone concentrations can be read directly.

9.2 If the DC amplifier is read directly, the reading must be converted to ozone concentration using the instrument calibration curve (8.6.3).

9.3 Conversion between p.p.m. and $\mu g./m.^3$ values for ozone can be made as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{m.^3} \times 5.10 \times 10^{-4}$$

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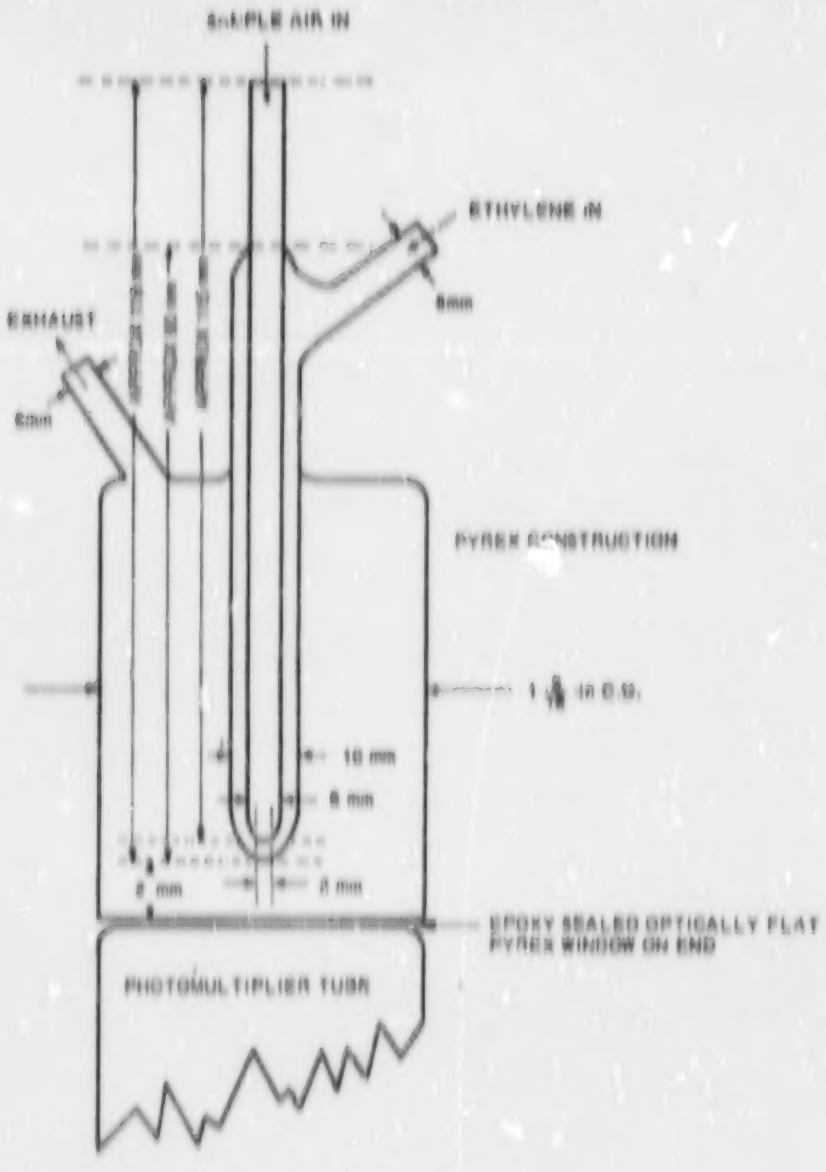

Figure D1. Detector cell.

[36 FR 22384, Nov. 25, 1971, as amended at 40 FR 7043, Feb. 19, 1975]

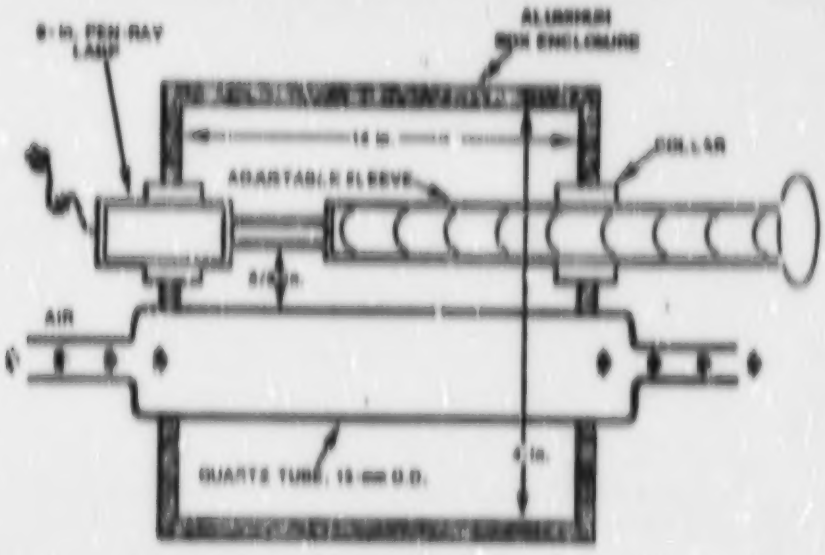

Figure D2. Ozone source.

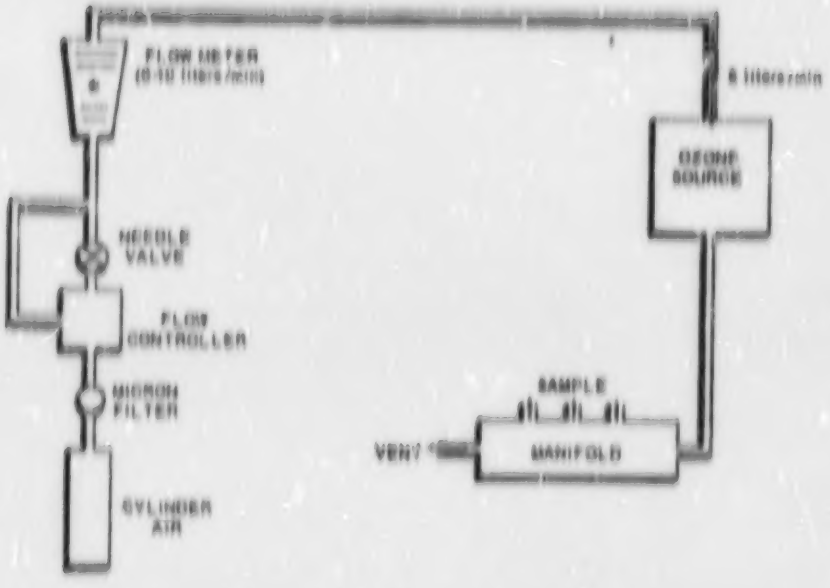

Figure D3. Ozone calibration air supply, source, and manifold system.

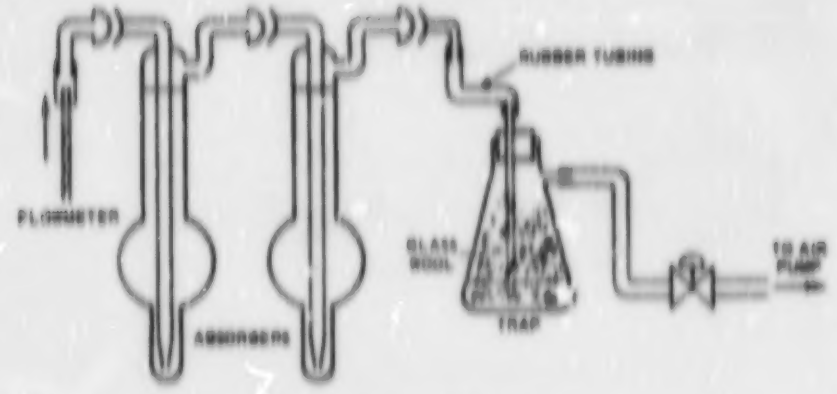

Figure D4 - SO2 sampling train.

[illegible]

A. *Suggested Performance Specifications for Atmospheric Analyzers for Hydrocarbons Corrected for Specific*

Range (minimum)	0.5 mg/m³ (0.2 ppm, THC) 0-5 mg/m³ (0-2 ppm, CH)
Output (minimum)	0-10 mv. full scale
Minimum detectable sensitivity	0.1 p.p.m. THC, 0.1 p.p.m. CH.
Zero drift (maximum)	Not to exceed 1 percent/24 hours
Span drift (maximum)	Not to exceed 1 percent/24 hours
Precision (minimum)	±0.5 percent
Operational period (minimum)	5 days
Operating temperature range (minimum)	0-40°C. to 90 percent
Operating humidity range (minimum)	
Linearity (maximum)	1 percent of full scale.

B. *Suggested Definitions of Performance Specifications*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full Scale—The maximum measuring limits for a given range.

Minimum Detectable Sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

Rise Time—The time required for a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

Time to 90 Percent Response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Lag Time (90 percent)—The interval between initial response time and time to 90 percent response after a step increase in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration, it is expressed as the average deviation of the single results from the mean.

Operational Period—The period of time over which the instrument can be expected to operate unattended within specifications.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Interference—An undesired positive or negative output caused by a substance other than the one being measured.

Interference Equivalent—The portion of indicated input concentration due to the presence of an interferent.

Operating Temperature Range—The range of ambient temperatures over which the instrument will meet all performance specifications.